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Formation of High Function Ceramic Surface by Ion Implantation

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SiC is a candidate material for advanced turbine engine component. It has superior characteristics such as higher hardness and elastic modulus than that of Si_3N_4. On the contrary, Si_3N_4 has better properties such as higher fracture toughness, oxidation–, and thermal shock-resistances. [1] If SiC-Si_3N_4 composite material can be made by using ion implantation technique, it can be served for multiple object. In this report, nitrogen ion was implanted into SiC and the chemical state of nitrogen as implanted and after heattreated was studied with XPS. The distribution of nitrogen implanted was measured with SIMS and RBS. The results were compared with the one by LSS theory.

1. INTRODUCTION

General properties required of a ceramic heat engine component were summerized as follows: [2] It requires to have thermal fatigue/thermal shock resistance, necessary temperature capability, adequate strength and creep behavior as a function of temperature and necessary longevity in the engine environment. In 1985, big project teems were organized for the saving import of petroleum in USA. [3] It was emphasized that the development of wear-resistant materials is important problem in the automobil industry.

In the past, many papers applied ion-implantation technique into ceramics have been presented. [4-10] As for SiC, the following main problems were discussed: 1) Amorphization effect, 2) In indentation test, pile-up and consequent exfoliation without cracking was observed when ion implanted, although circumferential and lateral cracking was occurred in unimplanted specimen, 3) Softening was induced with lower dose implantation, 4) Even the lowest dose of nitrogen chipping fracture was eliminated because of plastically deformation, 5) Unimplanted specimen remained hexagonal structure though highly deformed, but transformation to cubic form (β–SiC) occurred with ion implantation. However, there were no papers treated these phenomena from the structural viewpoint.

In this report, the authors have studied the change of distribution profile of nitrogen ion implanted with varying the accerelating voltage and after heattreatment temperature by using RBS and SIMS. The chemical state of nitrogen as implanted and after heattreated was studied with XPS. As an important problem it has been unsolved left whether the dissociation of SiC occurs or not when nitrogen was implanted and heattreatment was applied. Sufficient information to prove the dissociation behavior of SiC was obtained by using Raman spectroscopy.

2. EXPERIMENTAL PROCEDURE

The specimen used for ion implantation was pressureless SiC (Kyocera SC-201). After cut to be 80 x 10 x 3mm size, the slices were polished to 320-mesh for 1hr, 600-mesh for 0.5hr, and continuously to 100-mesh for 0.5hr on a series of laps and cloths. Further it was polished with boron powder of 1000-mesh for 1hr and of 1200-mesh for 0.5hr with the rotating velocity of 120/rpm under the load of 3kg. As finished stage, it was polished to 3μm diamond with same rotating velocity under the load of 1.5kg for

1.5hr. Surface finishing condition was observed with optical microscopy. Also the surface roughness was measured.

Ion implantation was performed with Kaufman type (thermal cathode). The dose rate was $10^{16} \sim 10^{18}$ ions/cm^2 and temperature of the specimen was kept to be 20°C. The background vacuum was 1.9×10^{-4} Pa. Especially, in this experiment, lower accerelating voltage was used for studying rather metallurgical than physical phenomena following with ion implantation. As accerelating voltage we have chosen 10, 20 and 30 kV. From the consideration of atom density of SiC, the implantation quantity was determined. The experimental conditions is given in Table 1.

For the heattreatment of ion implanted specimens, electric furnace composed from tungsten resistor which can be flowed nitrogen gas was used. Mixture gas composed from $N_2 + 5 \sim 8$mass%H_2 was flowed with the velocity of 16.7mm^3/s. From the preliminary test with the heattrearment conditions, it was confirmed that the dissolution of nitrogen ion implanted occurred above 1473K x 1hr. Therefore we have chosen heattrearment conditions shown in Table 2. To avoid the contamination of specimen during the heattreatment molybdenum sheet was used to cover the specimen.

In order to know the content of nitrogen implanted, we have used RBS(Rutherford Backscattering Spectroscopy). Experiment was done with a 1.5MeV He^+ beam delivered by the Van de Graaf accelerator. Incident beam diameter was 1mm. Under high vacuum of 5×10^{-7} Pa, we have measured with the scattering angle of 150° (ϕ_1=0°, ϕ_2=30°). Integrating time was 1000s for the unimplanted and 3600s for the implanted specimens, respectively. Moreover the comparison with the result obtained by LSS theory was done.

Because the real depth distributions of nitrogen atoms could not be determined by RBS, we have used SIMS (Secondary Ion Mass Spectroscopy). It has good sensitivity to detect lighter element such as nitrogen and it can measure less content implanted with weak accelerating voltage. Apparatus used for the measurement was Hitachi IMA-3 type analyser. O_2^+ was used as primary ion, and voltage of primary ion was 15kV. Sample current at sputtering was 0.1μA. Surface distribution content of nitrogen was compared with the ratio of Si-140. The distribution of nitrogen was determined with the relative value by SIMS and the absolute value by RBS.

To study the bonding state among silicon, carbon and nitrogen after implanted and heattreated as well as to investigate the oxidation advance at the surface after heattreated, we have applied XPS (X-ray Photoelectron Spectroscopy). The machine used was Shimadzu ESCA-750. The analysis was carried out with MgKα, and the scanning velocity of 0.1eV/s was used. The measurement of depth profile was done in combination with the sputtering by He ion. The energy scale was calibrated with C_{1s} peak.

The confirmation of free carbon due to the dissociation of SiC besides ion implantation was performed with Raman spectroscopic means. The apparatus used was Nippon Bunko R-800 type, and we have used argon ion laser. We have utilized 488.0 nm wavelength and the power was 500 mW. Repeated measurement of 8 times for the same specimen was applied during 150 – 2000 cm^{-1}.

Table 1 Ion implantation conditions

Accelerating voltage (kV)	N ion dose (ions/cm^2)
10	10^{17}
20	10^{16}
20	10^{17}
20	10^{18}
30	10^{17}

Table 2 Heat treatment conditions

temperature (K)	time (h)
773	1
873	1
973	1
1073	1
1273	1
1473	1

3. RESULT AND DISCUSSION

3.1 RBS spectrum

The RBS spectrum of unimplanted and ion implanted with 20kV IE17 is shown in Fig. 1(a) and (b). The mean depth implantation is 32.7nm at the case of 20kV and 43.5nm at 30kV. It was also determined the distribution width of 30.8 and 37.3nm respectively.

Further we have applied the modified LSS theory[11] which can calcutate ion implantation depth and the distribution width of the ion implanted. In Fig.2(a) and (b), the comparison of the experimental and calculated values is given. It is understood that the lower value at the mean project range and higher value at the standard deviation is obtained.

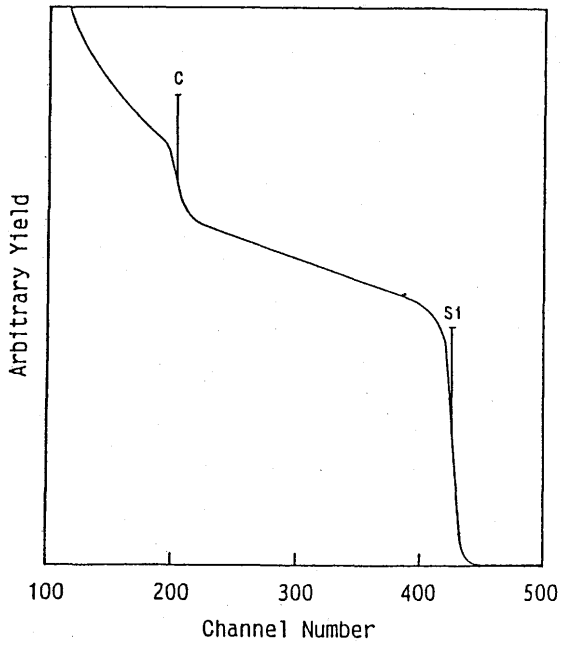

Fig. 1 (a) RBS spectrum of unimplanted PLS SiC

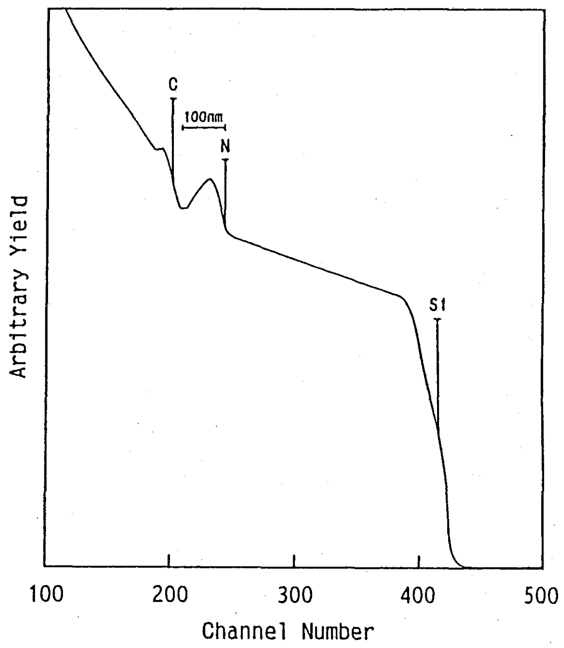

Fig. 1 (b) RBS spectrum of nitrogen ion implanted PLC SiC (20kV, 1E17ions/cm^2)

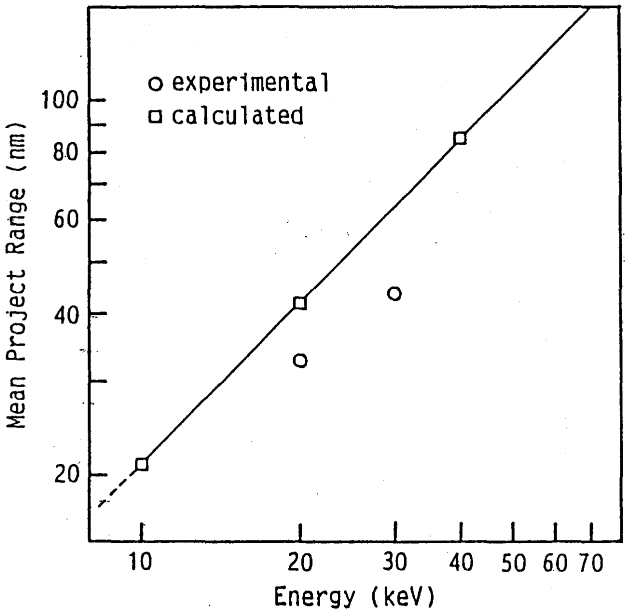

Fig. 2 (a) Comparison of mean project range calculated by LSS theory with experimental values

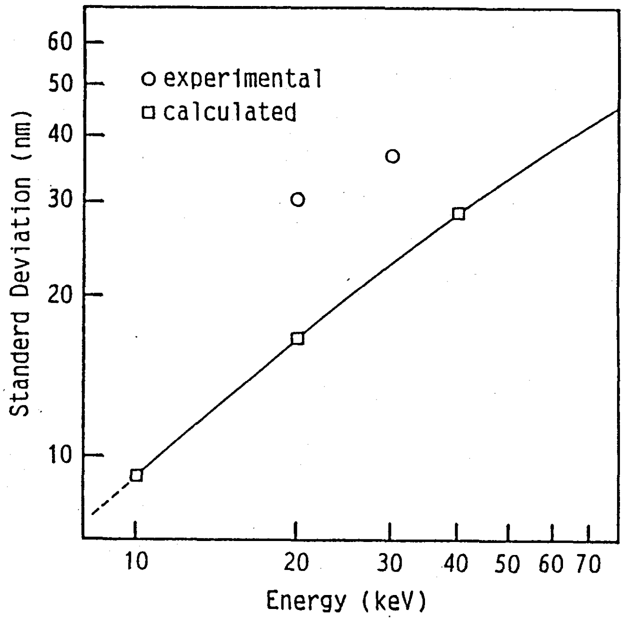

Fig. 2 (b) Comparison of standard deviation calculated by LSS theory with experimental values

3.2 SIMS results

Of course, the SIMS results showed that the higher accelerating voltage, the deeper ion implantation becomes. In Fig. 3, the variation of depth profile of nitrogen atom implanted with the change of after heattreatment temperature is shown. It can be confirmed that the migration of nitrogen ion towards surface becomes greater with the increase of after heattreatment temperature. Also it was certified that a great deal of nitrogen was released with the heattrearment above 1273K, and there are no remaining nitrogen above 1473K.

3.3 XPS results

In Table 3, the comparison of the Si_{2p} levels for the specimens, nitrogen ion implanted with varying the accelerating voltage, unimplanted, and the standard Si_3N_4 is given. Fig. 4 (a) and (b) shows the changes in the Si_{2p} peak with the increase of after heattreatment temperature. As temperature increases, the intensity of 103eV peak increases and, on the other hand, the intensity of 101.1eV decreases. It is perhaps due to the formation of SiO_2 at the surface with the higher after heattreatment temperature. While at higher implanted concentration the shift occurrance to 103.2eV can be attributed to the formation of $Si_xO_yN_z$. The remarkable difference between 1E16 and 1E18 specimens is with and without double peak appearance.

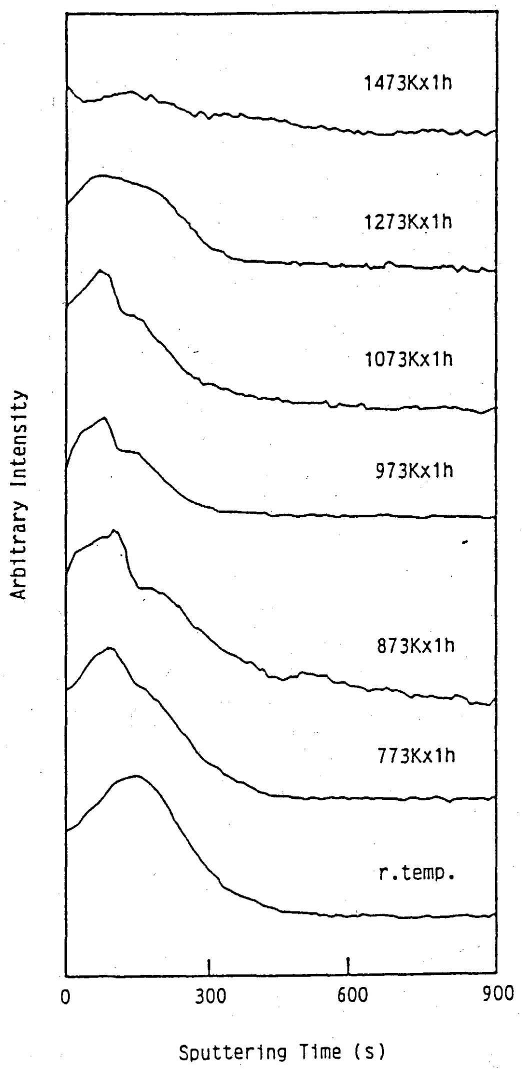

Fig. 3 Change of ^{14}N depth profile with heattreatment (20kV, 1E18ions/cm^2)

Table 3 The comparison of the Si_{2P} levels for the specimens

Specimen	Ion implantation condition		Binding energy of Si_{2P} (eV)
	Accelerating voltage (kV)	N ion dose (ions/cm²)	
Si_3N_4	Non-implantation		102.4
SiC	Non-implantation		101.1
	10	10^{17}	102.2
	20	10^{16}	100.7
	20	10^{17}	101.9
	20	10^{18}	102.1
	30	10^{17}	101.7

(after sputtering for 600s)

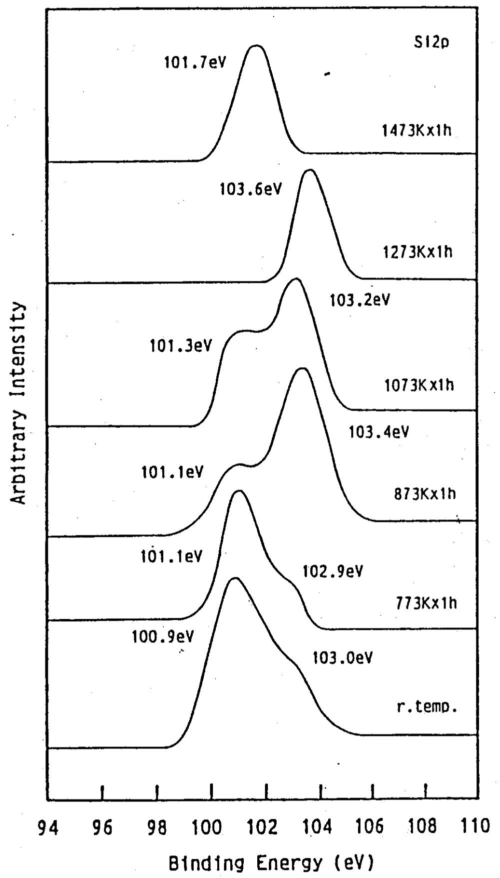

Fig. 4 (a) Relationship between Si_{2p} spectrum and heattreament temperature (20kV, 1E16ions/cm² : before sputtering)

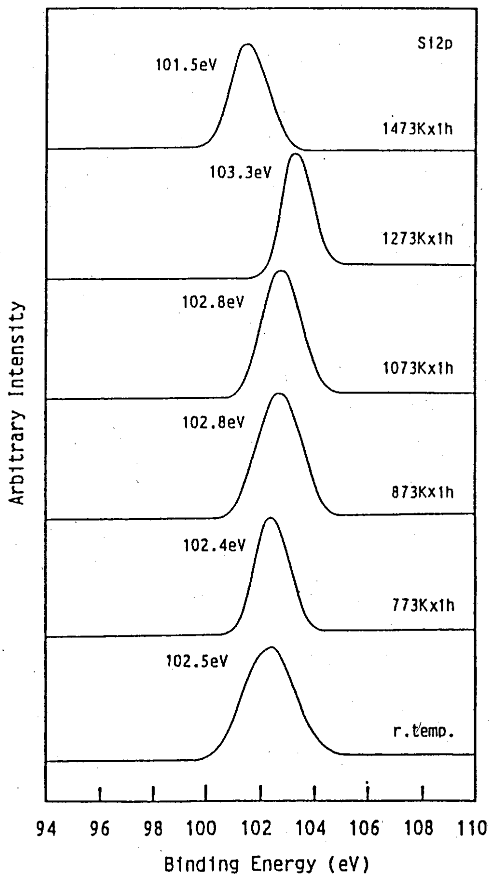

Fig. 4 (b) Relationship between Si_{2p} spectrum and heattreatment temperature (20kV, 1E18ions/cm²: before sputtering)

The formation of SiO_2 at the heattreatment of 1273K is consistent with the result by SIMS that the intensity of nitrogen decreases in the near temperature of the heattreatment. Further we have found that the shift of Si_{2p} peak from 101 to 102.5eV occurred with the increase of implantation dose. With the heattreatment above 1473K, Si_{2p} peak shows SiC from the dissolution of nitrogen implanted. In Fig. 5 (a) and (b), the information of inside of specimen after heattreated is given. At the case of 1E16 specimen, the oxidation proceeds inside of specimen, but other specimens implanted higher dose of nitrogen did not show the indication of inside oxidation. In Fig. 6, the variation of N_{1s} peak with the change of after heattreatment temperature is shown. The assessment of 398eV peak exhibits the formation of Si_3N_4 and the same result was confirmed in all cases, but the disappearance of 400eV peak was noticed with higher after heattreatment temperature. The assessment of this peak was made by previous experiment for free nitrogen or compound NO.[12] While SIMS result illustrates that some nitrogen atom could not migrate towards surface with the heattreatment. Taking this into account, the peak of 400eV can be identified in terms of the formation of free nitrogen in the specimen implanted.

In order to know the occurrence of dissociation of SiC with nitrogen ion implantation, the comparison of the Raman spectroscopic profile between ion implanted and unimplanted specimens was performed. The result is shown in Fig. 7. As for the specimen ion implanted, the appearance of broad peak ranging from 1300 to 1650 cm^{-1} which can be attributed to the formation of free carbon was confirmed. In Fig. 8 (a) and (b), the variation of Raman spectroscopic profile by changing after heattreatment temperature is given. The observed peak splitting to 1300 and 1600 cm^{-1} accounts for the formation of graphite[13]. As the increment of the heattreatment temperature, the intensity of these peaks increases. It means that higher after heattreatment temperature contirbutes to the progress of crystallization of free

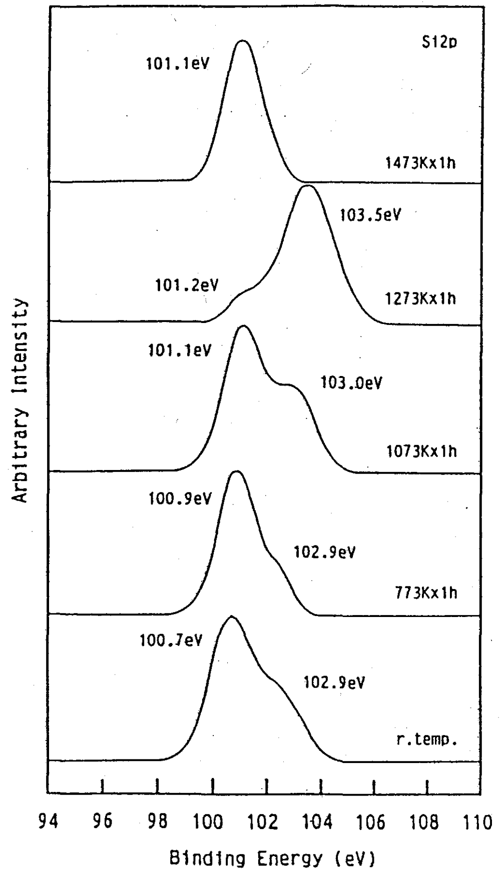

Fig. 5 (a) Relationship between Si_{2p} spectrum and heattreatment temperature (20kV, 1E16ions/cm^2: after sputtering for 600s)

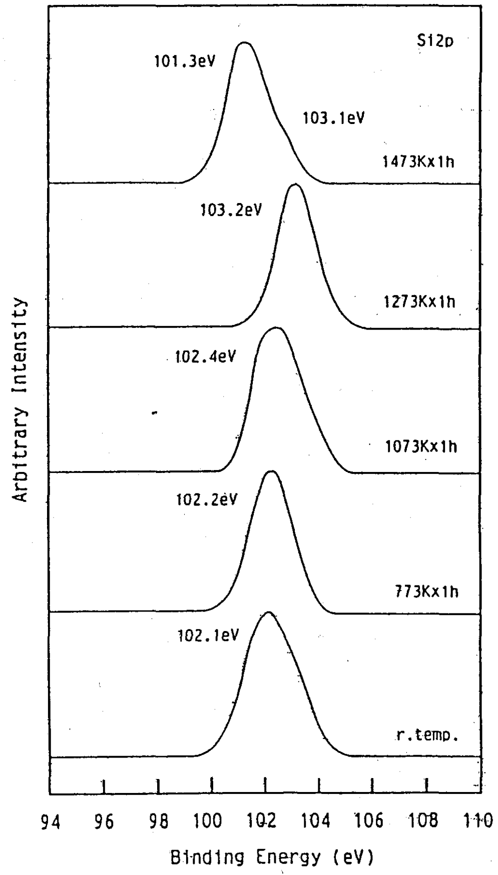

Fig. 5 (b) Relationship between Si_{2p} spectrum and heattreatment temperature (20kV, 1E18ions/cm^2: after sputtering for 600s)

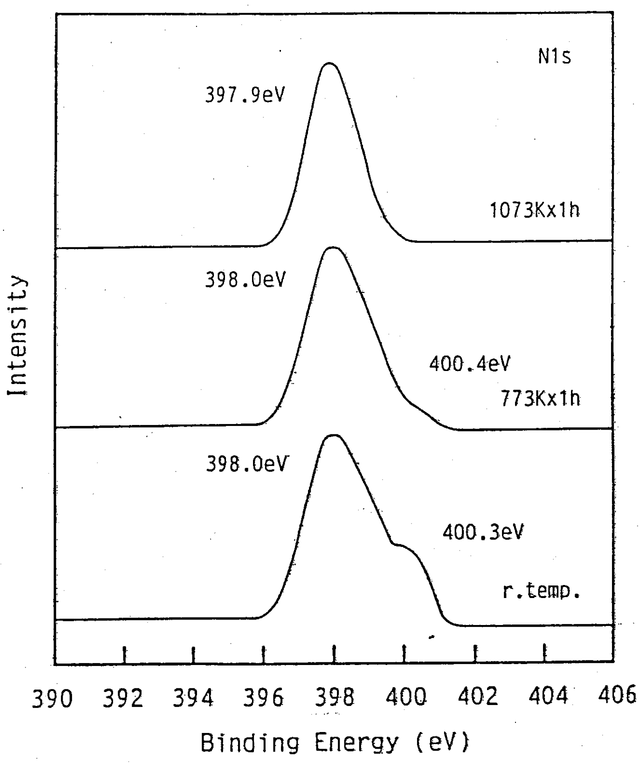

Fig. 6 Relationship between N_{1s} spectrum and heattreatment temperature (30kV, 1E17 ions/cm^2: after sputtering for 600s)

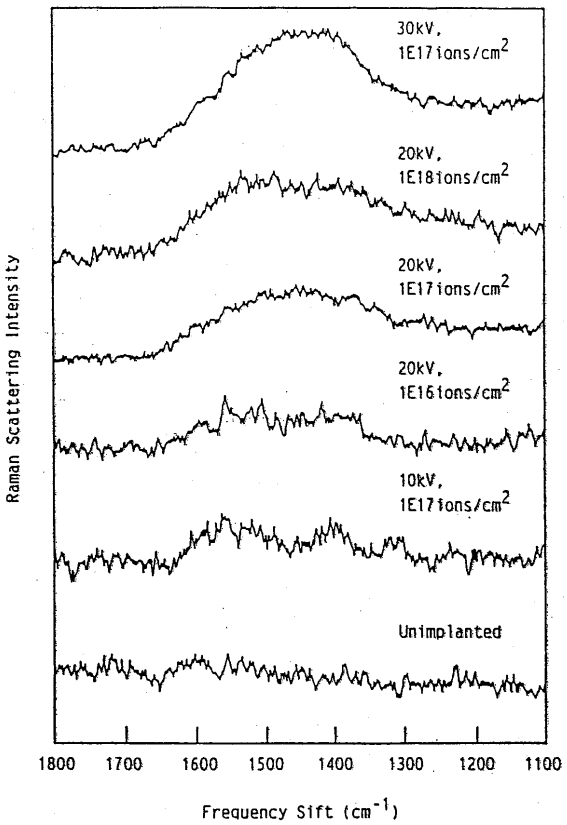

Fig. 7 Change of carbon Raman spectrum with ion implantation conditions

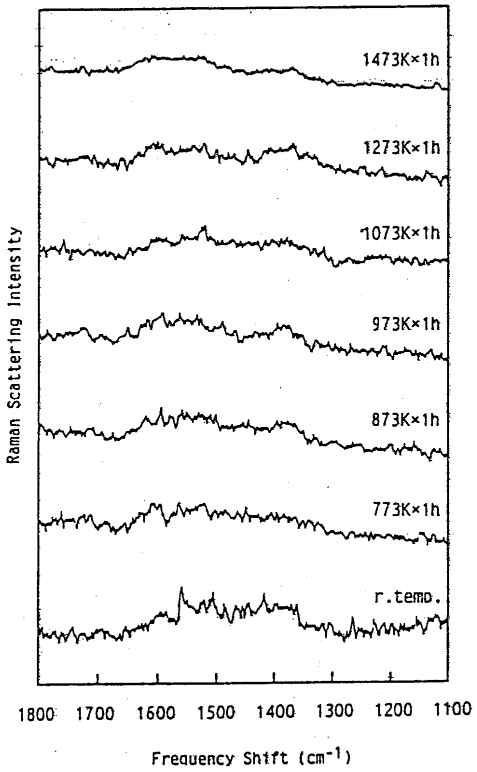

Fig. 8 (a) Change of carbon Raman spectrum with heattreatment temperature (nitrogen ion: 20kV, 1E16ions/cm^2)

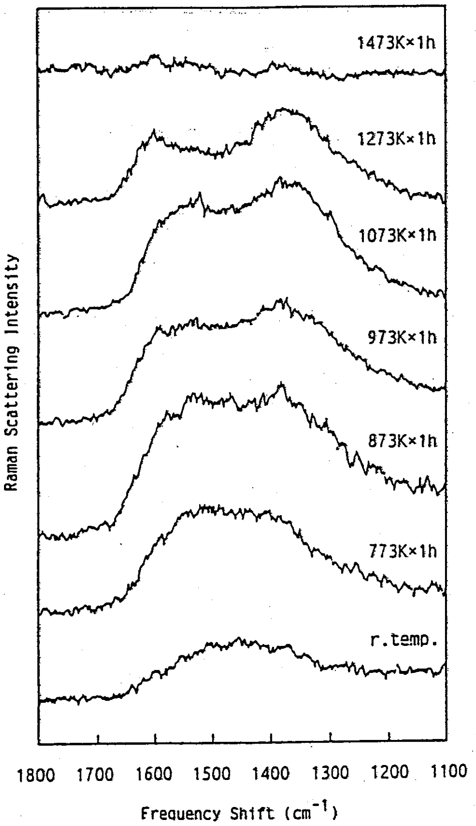

Fig. 8 (b) Change of carbon Raman spectrum with heattreatment temperature (nitrogen ion: 20kV, 1E17ions/cm^2)

carbon. The corresponding information was obtained in the case of after heattreatment at 1473K with unimplanted specimen. This means that the evolution of nitrogen, oxygen and free carbon dissociated from SiC occurs from the surface of specimen with higher after heattreatment temperature. The result is consistent with the one obtained by XPS.

4. SUMMARY

State change of nitrogen ion implanted into SiC was confirmed with XPS and the possibility of the dissociation of SiC with ion implantation and after heattreatment was also examined with XPS and Raman spectroscopy. The results obtained are as follows:

1) Nitorgen ion implantation was accurately carried out.
2) Migration of nitrogen inside implanted occured with after heattreatment. Some nitrogen exhibited the lower migration velocity, and they were considered as combined nitrogen.
3) Depending on the implantation condition, the occurence of the formation of carbonitride. It was confirmed that the lowering of crystallinity of SiC occurs with ion implantation.
4) At the case of specimen to easily form carbonitride, oxidation occurred only at the surface, and free carbon crystallises with the heattreatment.
5) With the heattreatment above 1473K, oxide and nitride evolves from surface.

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